炭酸塩構造置換態硫酸の同位体比分析によるエディアカラ紀ドウシャントフォーメーションの硫黄循環の解明

Ediacaran sulfur cycling reconstructed from an isotopic analysis of carbonate associated sulfate in Doushantuo Formation

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Carbonate associated sulfate (CAS) is useful for reconstructing sulfur isotopic composition of seawater sulfate. However, extraction method of CAS from carbonate rocks has not been firmly established yet. In particular, oxidation of co-existing pyrite sulfur would seriously damage isotopic analysis of CAS during the extraction from rock samples. We have developed an improved method to extract the pure CAS and evaluated the validity of the new method using scallop shell powder containing modern marine CAS and pyrite powder. The results demonstrate that the new CAS extraction method is effective for preventing unwanted sulfur components from co-existing pyrite when the pyrite/CAS ratio in a sample is <10. We applied the new CAS extraction method to Ediacaran drill core samples from the Three Gorges area, South China collected by a Tokyo Tech.–Xian Univ. joint project. The studied section includes the Neoproterozoic Doushantuo Formation and the overlying Dengying Formation. The concentrations of CAS from the Doushantuo and Dengying Fms. range from 0 to 365 ppm with an average value of 105 ppm. The $\delta^{34}S$ values of CAS range from +24 to +46‰ with an average value of +34‰. A previous study of the Doushantuo samples collected from outcrop reported that the CAS concentrations range from 0 to 2159 ppm with an average value of 570 ppm (n=73), and the $\delta^{34}S$ values of CAS range from +7 to +44‰ with an average value of +25.7‰ (n=83) (McFadden et al., 2008). The apparent differences between the present and previous data may indicate that the careful treatment is nessesary during CAS extraction. Based on the new sulfur isotope data of CAS and of chromium reducible sulfur (CRS) (n=44), we reconstructed the Neoproterozoic sulfur cycle in Three Gorges area. The difference of $\delta^{34}S$ value between CAS and co-existing CRS increased from 5‰ at the Doushantuo cap carbonate, +26‰ in the Member 2, and exceeded 40‰ in the Member 3 of the Formation. The maximum sulfur isotope fractionation between CAS and co-existing CRS exceeded 47‰ in the Member 3. The fractionation between CAS and CRS decreased down to -3‰ at the Dengying Formation. This suggests that sulfate concentration increased at the upper part of Doushantuo Fm.; however, decreased again before Dengying Formation. In addition, our quadruple sulfur isotope analysis revealed that mass-dependent-exponent for 36S (lambda-36 value) between CAS and CRS is relatively constant around 1.90, regardless of the degree of δ34S isotope fractionation. This indicates that the Ediacaran sulfur cycle in Three Gorges area is markedly different from modern marine sulfur cycling.

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